HYDROGEN PRODUCTION FOR FUEL CELLS VIA REFORMING COAL-DERIVED METHANOL

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DISCLAIMER

ABSTRACT

Hydrogen can be produced from many feed stocks including coal. The objectives of this project are to establish and prove a hydrogen production pathway from coal-derived methanol for fuel cell applications.

This progress report is the fifth report submitted to the DOE reporting on the status and progress made during the course of the project. This report covers the time period of October 1 – December 31, 2004. This quarter saw progress in four areas. These areas are:

1. Degradation tests using bluff bodies,
2. Autothermal reforming of coal derived methanol,
3. Catalyst deactivation,
4. Steam reformer transient response.

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EXECUTIVE SUMMARY

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This progress report is the fifth report submitted to the DOE reporting on the status and progress made during the course of the project. This report covers the time period of October 1 – December 31, 2004.

Much progress has been made on the project funded by the Department of Energy during this reporting period. All of the projects are proceeding on or slightly ahead of schedule. This quarter saw progress in four areas. These areas are:

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2. Autothermal reforming of coal derived methanol,
3. Catalyst deactivation,
4. Steam reformer transient response.

Degradation tests have begun using the flow disturbance disks and rings sets referred to as bluff bodies. As the bluff body set up has shown increased conversion of fuel as noted in past reports, it is expected that the flow disturbers will also have an effect in decreasing catalyst degradation rates. The first set of data has been collected regarding the use of coal based methanol with the bluff body set up. The degradation rates are much higher in this reactor than with the previous smaller reactors used for testing catalyst deactivation. In comparison to catalyst degradation due to the differences in fuel type (fuel cell grade vs coal derived methanol) as reported previously, it appears that the effect of reactor geometry on catalyst degradation far outweighs the effect of fuel type. This is an encouraging result for those eager to use coal-derived methanol as a hydrogen feed-stock. Future work is necessary to further quantify the effect of geometry in catalyst degradation.

Autothermal reforming of coal-derived methanol has taken place with a low grade catalyst. Initial findings show that reactor performance was similar to fuel cell grade methanol. Analysis of the results is continuing and further tests will be made with a specialty catalyst.

We have begun investigating the role of temperature in catalyst deactivation in order to understand how geometry can play such a large role in this important parameter. Tests with quasi-isothermal reactors quantify the large dependence of catalyst degradation on temperature. This reinforces the idea that minimizing temperature gradients within the reactor can be as important to the steam reformation process as fuel purity, if not more so. Work continues on investigating the role of temperature.

In addition to the above projects in steam reformation using the coal derived methanol, work with quantifying the transient response is also taking place. This is currently being done with fuel cell grade methanol and will progress with coal derived methanol shortly.

Several projects are scheduled for the next quarter including further ATR reactor development and testing, continued evaluation of coal-based methanol in the steam reformers, transient testing and measuring catalyst degradation using the various methanols. We also plan to evaluate various clean-up options for the reformate and how to direct the clean hydrogen stream to the PEM fuel cell.

EXPERIMENTAL

The following section describes the experimental methods used and developed during the reporting period for the following areas: degradation tests using bluff bodies, autothermal reforming of coal derived methanol, catalyst deactivation, and steam reformer transient response.

Degradation Tests Using Bluff Bodies

This experiment used Reactor B as a base reactor to investigate the catalyst degradation rate under a passive flow in the catalyst bed. Reactor B was packed with eight packages of bluff bodies using a crushed copper-based catalyst. Chemical-grade methanol was used as the reforming fuel for this degradation experiment. In the coming experiments, reactor B with no bluff body packages will be tested with the same conditions to investigate reactor geometry effects on the catalyst degradation rate. The coal-derived methanol will also be used for further analysis. The crushed catalyst had an average length of 0.25 cm (0.098 in). A 30-hours experiment was conducted with an 80-minute data point interval to measure the real time methanol conversion. The mass of the catalyst used in the experiment was 250 grams (.551 lb) packed in Reactor B, shown in Figure 1.

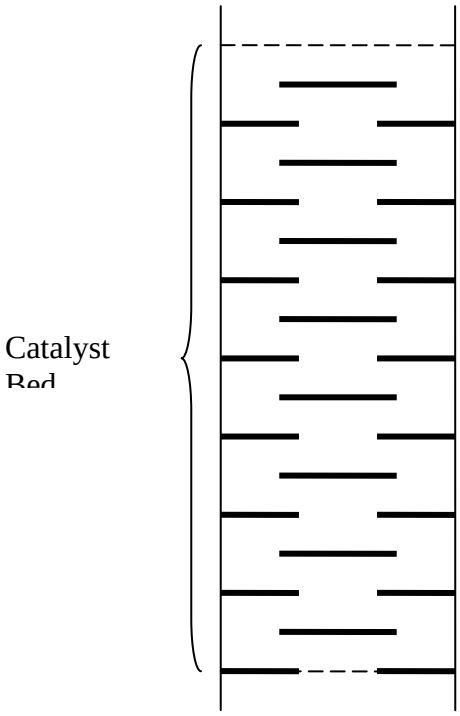

Figure 1: Layout of eight bluff body packages inside reactor B

Autothermal Reforming of Coal-Derived Methanol

The autothermal reforming of coal-derived methanol test was initiated by using "Urban catalyst." The catalyst used in this experiment was taken from an automotive catalytic converter. A catalytic converter in a car is used to reduce harmful emissions from the engine exhaust. Inside a catalytic converter there are two monolithic catalysts, one located upstream and the other downstream. The one located in the upstream position plays as a reduction catalyst. It contains platinum and rhodium, which helps reduce the NOx emissions. The oxidization catalyst located downstream contains platinum and palladium, which can reduce the unburned hydrocarbon and carbon monoxide by burning them with oxygen. This experiment adopted the oxidization catalyst as an ATR catalyst to test its function as a catalyst for coal-derived methanol. The catalyst was machined into a cylindrical shape with a length of 3.713 cm (1.462 in) and 3.78 cm (1.330 in) diameter, shown in Figure 2.

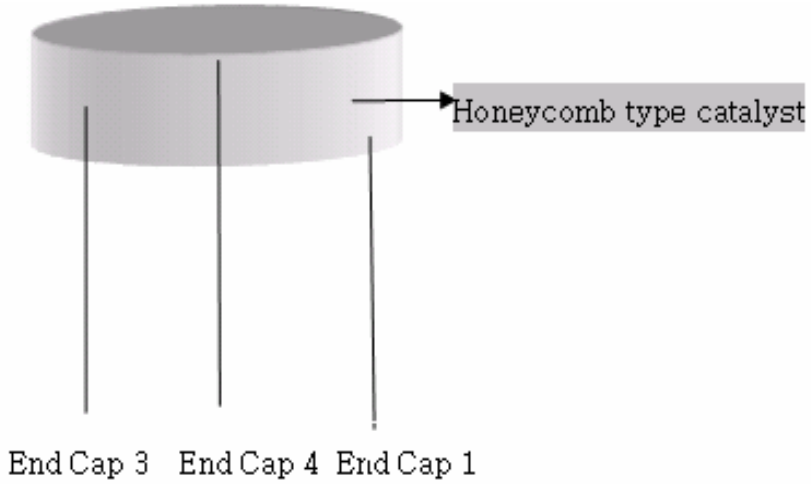

Figure 2: The location of end-cap thermocouples

Catalyst Deactivation

During the reformation process, the catalyst will slowly lose effectiveness to a point where the methanol conversion drops below an acceptable level and the catalyst must be replaced. Since the catalyst is a major contributor to the cost of a reformer, it is beneficial to be able to estimate how long the catalyst will last. In this study, the rate of catalyst deactivation in steam reformation of methanol is measured under steady-state, isothermal conditions over a range of temperatures and flow rates. The goal is to obtain information that can be used to estimate the lifetime of a non-isothermal catalyst bed from its temperature profile. During the first phase of the study, the conversion percentage was measured over a 7.5 hour period at intervals of 1.5 hours. All runs were performed with reactor A containing a mixture of crushed catalyst and inert material. Both the catalyst and inert particles were sieved to be between 0.159 cm (1/16 in) and 0.3175 cm (1/8 in) in diameter. The amount of catalyst used in each run was chosen by

estimating the amount required to fully convert 2.0 ml/min (0.0676 oz/min) of premix at the temperature for the run. The range of temperatures studied was from 190^{o} C (374^{o} F) to 350^{o} C (662^{o} F), which covers the range that can occur within a small non-isothermal reactor. The range of flow rates studied was from 2.0 ml/min (0.0676 oz/min) to 2.6 ml/min (0.0879 oz/min). It is expected that there is a small range of temperature over which catalyst deactivation is minimized, with an increase in deactivation at temperatures above and below the optimal range. Furthermore, it is expected that flow rate should have at least a secondary effect on deactivation.

Steam Reformer Transient Response

For practical applications of small-scale reformers, transient response is just as important to reactor performance as steady-state conversion. Steam reformation is known to have a relatively slow transient response due to heat transfer limitations, so it is beneficial to understand the behavior of steam reformers under transient flow conditions and find ways to improve the response time. In this experiment, observations were taken as the reactant flow rate through a steam reformer was cycled between a low rate and a high rate. The experiment was performed on reactor B filled with 250g (.551 lb) of crushed catalyst. The flow rate varied from 2.5 ml/min (0.0845 oz/min) to 5 ml/min (0.169 oz/min), changing every 15 minutes, which allowed the reactor to reach steady state before the next change in flow rate. Based on previous experiments, the steady-state conversion at both flow rates should be nearly 100%. However, 5 ml/min (0.169 oz/min) is close to the maximum flow rate where 100% conversion can be achieved. It is expected that when the flow increases to 5 ml/min (0.169 oz/min), the reactor will not be able to respond immediately, so some methanol will remain unconverted until the reactor can heat up enough to reach 100% conversion.

RESULTS AND DISCUSSION

The following section presents results from the reporting period from the following areas: degradation tests using bluff bodies, autothermal reforming of coal derived methanol, catalyst deactivation, and steam reformer transient response.

Degradation Tests Using Bluff Bodies

Catalyst degradation test associated with different reactor geometries were initiated using chemical grade methanol, which is to be compared with similar experiments using coal-derived methanol. This test was performed on Reactor B and included bluff bodies. The different geometry of the reactors might cause different degradation rates due to different heat and mass transfer limitations. Through this degradation test, we expected to be able to construct an experimental degradation matrix in terms of limitations associated with different reactor geometry, such as aspect ratio and different zones of the catalyst being active within the catalyst bed. Therefore, this result is extremely important from the standpoint of the design of an optimized steam reforming reactor to be used for fuel cell applications. This experiment was performed using the fixed dependant variables of space velocity [2.5(1/hr)] and inlet temperature [250^{o} C (482^{o} F)] in order to allow for a comparison with previous degradation results. At this time, chemical grade methanol was used with deionized water at a 1.5:1 steam carbon ratio.

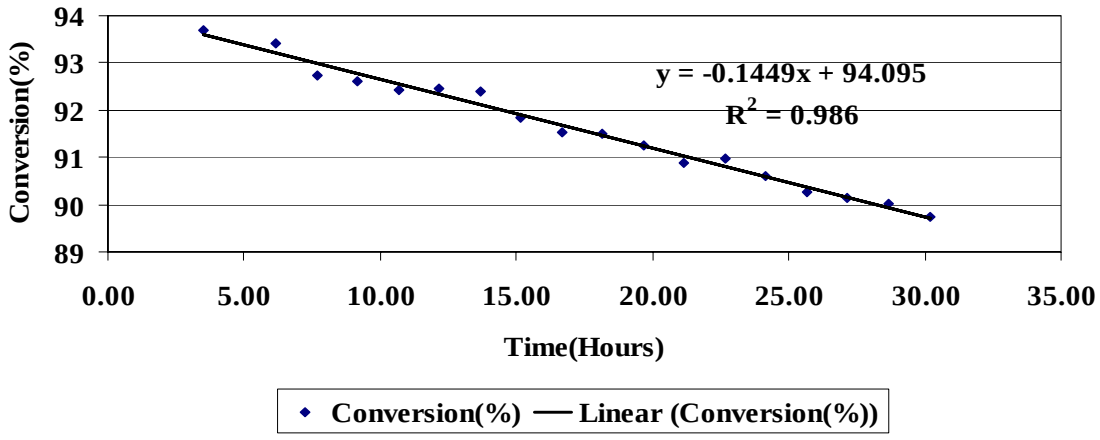

Figure 3: Catalyst degradation test in Reactor B using bluff bodies

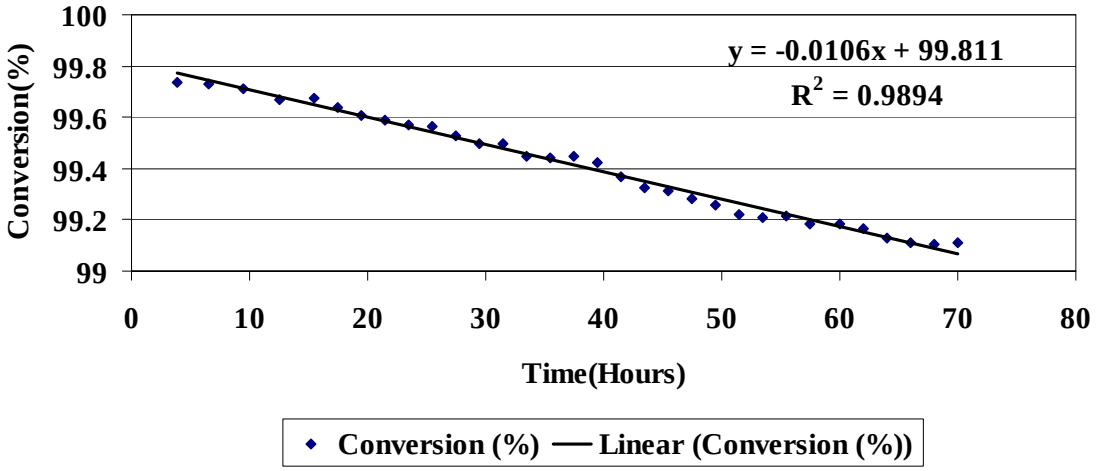

Figure 4: Catalyst degradation test in Reactor C using internal cartridge heater

As seen in Figure 3 a -0.1449% per hour degradation rate was shown in Reactor B with bluff bodies. The above results are compared to previous data, which was performed on reactor C with an internal cartridge heater as shown in Figure 4. The degradation rate of reactor B was almost ten times greater than that of Reactor C even though 250g (.551 lb) of crushed catalyst [39g (.086 lb) of crushed catalyst loaded in reactor C] was loaded in reactor B with bluff bodies. In the previous report, it was confirmed that bluff bodies enhance the steam reforming reaction due to the promotion of heat transfer as well as mass transfer associated with passive mixing effects. In other words, passive enhancement mixing using bluff bodies can also increase the methanol overall conversion compared to a non-bluff body reactor. We also confirmed that active enhancement of heat and mass transfer using an internal cartridge heater also can promote increases in overall conversion as well as decreases in catalyst degradation. However, in the degradation test of reactor B (passive enhancement) showed the weakness of degradation compared to reactor C (active enhancement using the cartridge heater). Reactor B had a larger amount of catalyst than reactor C thereby also having more catalytic active space than reactor C. In other words, more reactive space through radial and axial directions can lead to the aggravation of heat and mass transfer limitation because heat is only supplied from the exterior heat band. Consequently, even though passive enhancement using bluff bodies promoted heat and mass transfer, it might not be enough to supply the heat demand in reactor B for long-term operation.

If bluff bodies were used in a small diameter reactor such as reactor A, it might have a more profound effect than bluff bodies in reactor B. In contrast, the heat requirement areas for steam reforming reaction of reactor C were much smaller than those of reactor B because of its diameter and length (aspect ratio). Furthermore, an internal cartridge heater was placed in the center of the reactor so that heat was supplied from both the interior and the exterior of the catalyst bed.

In summary, we confirmed that different reactor geometry is a large factor that contributes to catalyst degradation. Better heat and mass transfer through smaller axial

and radial length can suppress the catalyst degradation rate in terms of durability of the catalyst.

In comparison to catalyst degradation due to the differences in fuel type (fuel cell grade vs coal derived methanol) as reported previously, the effect of reactor geometry on catalyst degradation far outweighs the effect of fuel type. This is an encouraging result for those eager to use coal-derived methanol as a hydrogen feed-stock. Future work is necessary to further quantify the effect of geometry in catalyst degradation.

Autothermal Reforming of Coal-Derived Methanol

Autothermal reforming of Coal derived methanol has taken place. The catalyst was wrapped with insulation and placed at Zone 4 of the ATR reactor as shown in Figure 5.

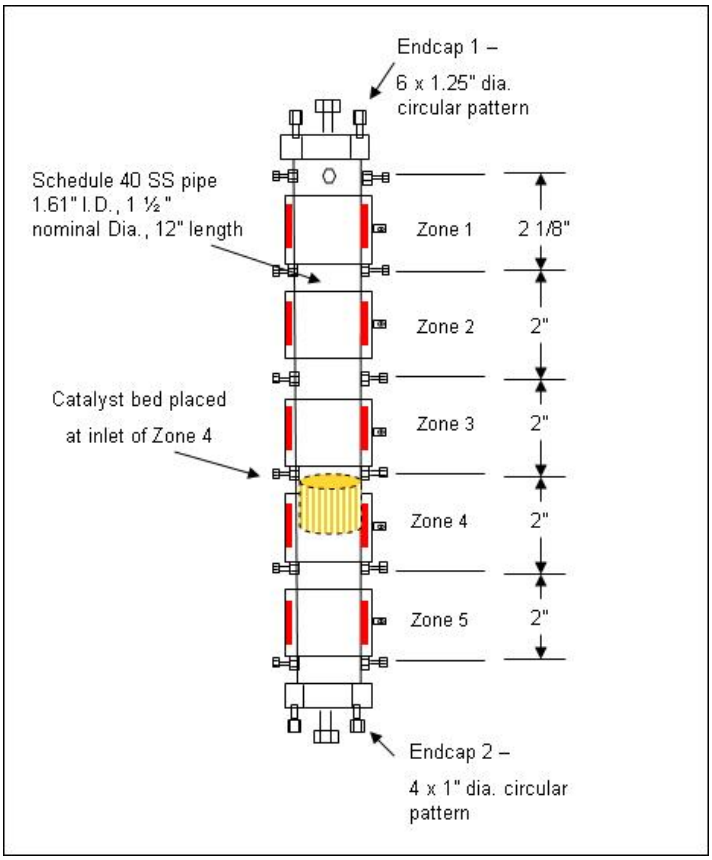

Figure 5: Location of monolithic catalyst inside ATR reactor

Different gas hourly space velocities (GHSV) were applied based on different O_2/C ratios. The GHSV and O_2/C ratio were calculated via the developed ATR model, which uses the premix flow rate and airflow rate into the reactor and the operating pressure of the experiment as inputs. Since the premix used for the experiment was fixed with a steam/carbon ratio with 1.5:1, the carbon mole number was fixed through out the experiment run by fixing the premix flow rate into the ATR reactor. By changing the

airflow rate into the reactor, the O_2 mole number was increased thus the O_2/C ratio increased. As shown in Figure 6, as GHSV and O_2/C ratio increased, methanol percent conversion was linearly increased.

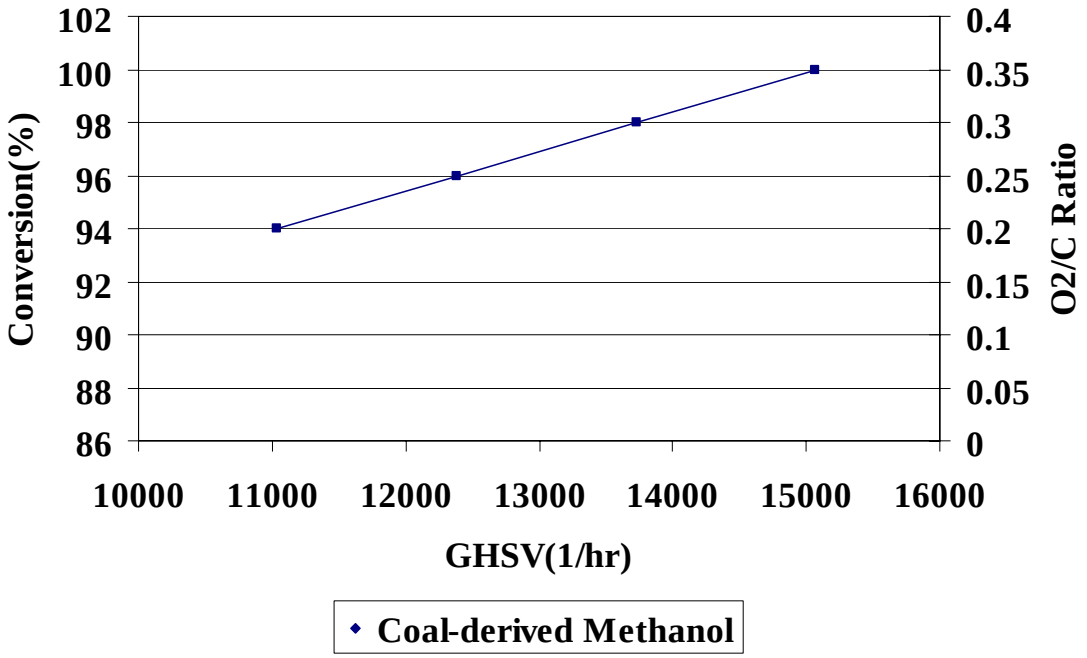

Figure 6: Autothermal reforming of coal-derived methanol varying O_2/C ratios at a flow rate of 8.5ml/min

The O_2/C ratio was increased up to 0.4 causing the catalyst to sinter, because higher O_2 can bring higher temperature caused by combustion of O_2 and CH_3OH.

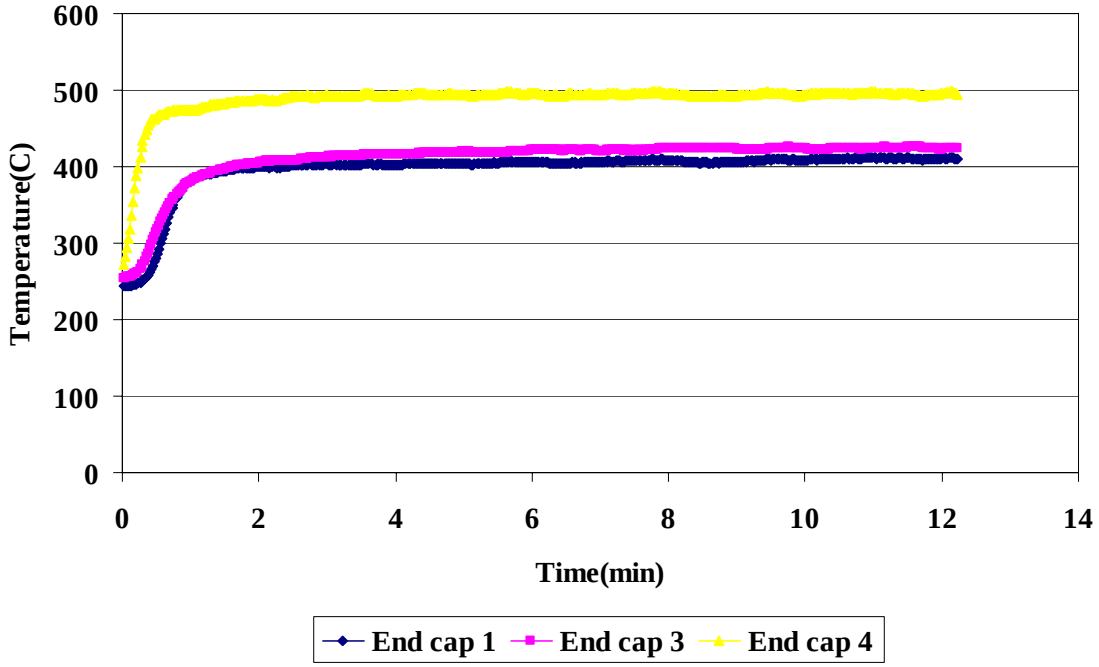

Figure 7: Temperature profile inside the urban catalyst at different locations (O_2/C=0.2)

Light-off was confirmed by the end-cap thermocouples located inside the catalyst as seen in Figure 2 and Figure 7. Light-off occurred near the top surface of the catalyst. The temperature was increased from 250 C^o (482^o F) to 500 C^o (932^o F) at the top surface. In the middle and bottom zones of the catalyst, the temperature was increased less than approximately 150 C^o (302^o F) due to chemical reaction. In other words, heat generated from light-off was consumed for the steam reforming reaction as well as methanol decomposition inside the catalyst. That is why the temperature decreased at each reaction zone.

Catalyst Deactivation

Although the catalyst deactivation study is still in progress, data has already been collected which shows some interesting trends (Table 1). Figure 8 shows the methanol conversion rate normalized to the amount of catalyst in the reactor. Using linear regression, the rate of deactivation was determined. Figure 9 shows the rate of deactivation normalized to the initial rate of conversion. Based on current data, the best operating temperature to maximize catalyst lifetime is around 290C (554^o F), where the deactivation rate is 0.37% per hour. Lower operating temperatures increase the deactivation rate to 1.35% per hour at 250C (482^o F). Higher operating temperatures also increase the deactivation rate, but to a much greater extent. Additional experiments will further characterize the effects of both temperature and flow rate on catalyst deactivation.

Table 1: Data from catalyst deactivation study

Temp (C)	Cat (g)	Flow (ml/min)	Conversion after X hours online					
			0	1.5	3	4.5	6	7.5
250	14	2.6	88.0%	86.1%	84.1%	82.8%	80.7%	79.1%
270	13	3.2	83.8%	82.0%	81.2%	80.1%	79.2%	78.0%
290	5.4	2.6	67.6%	68.6%	69.0%	67.7%	67.8%	65.7%
310	3.6	2.6	71.5%	69.2%	68.2%	66.4%	65.0%	63.3%
350	2.7	2.6	65.9%	58.2%	53.0%	48.7%	45.5%	42.6%

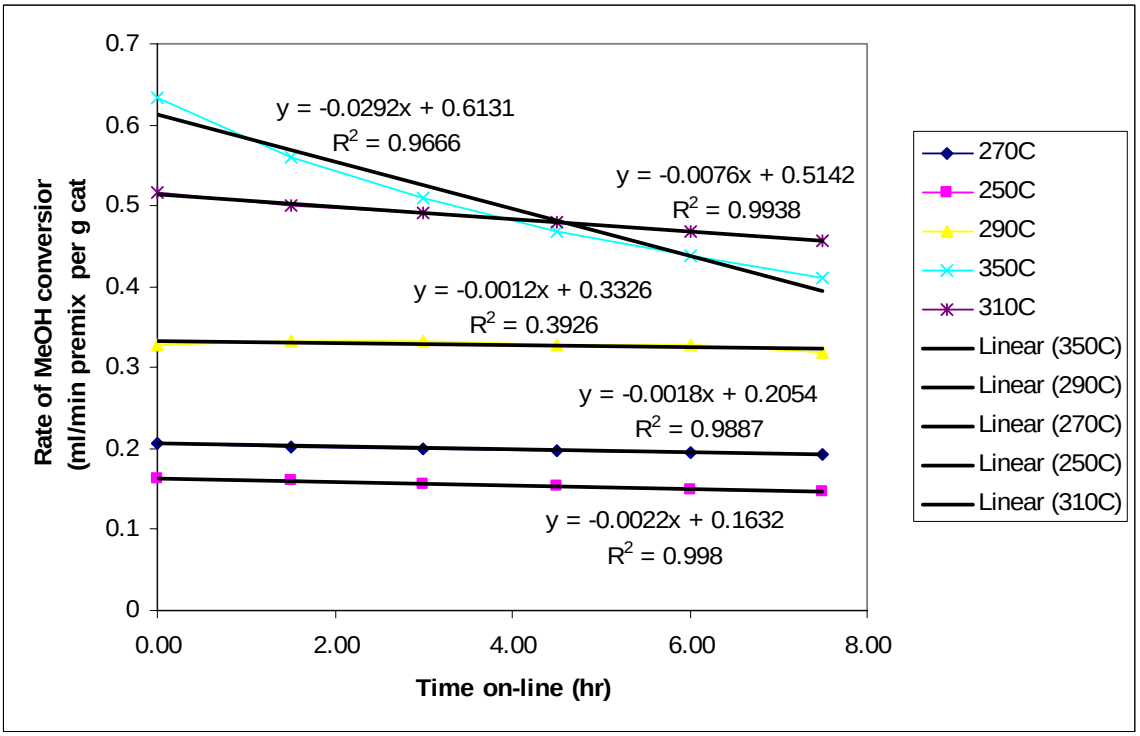

Figure 8: Change in methanol conversion over time

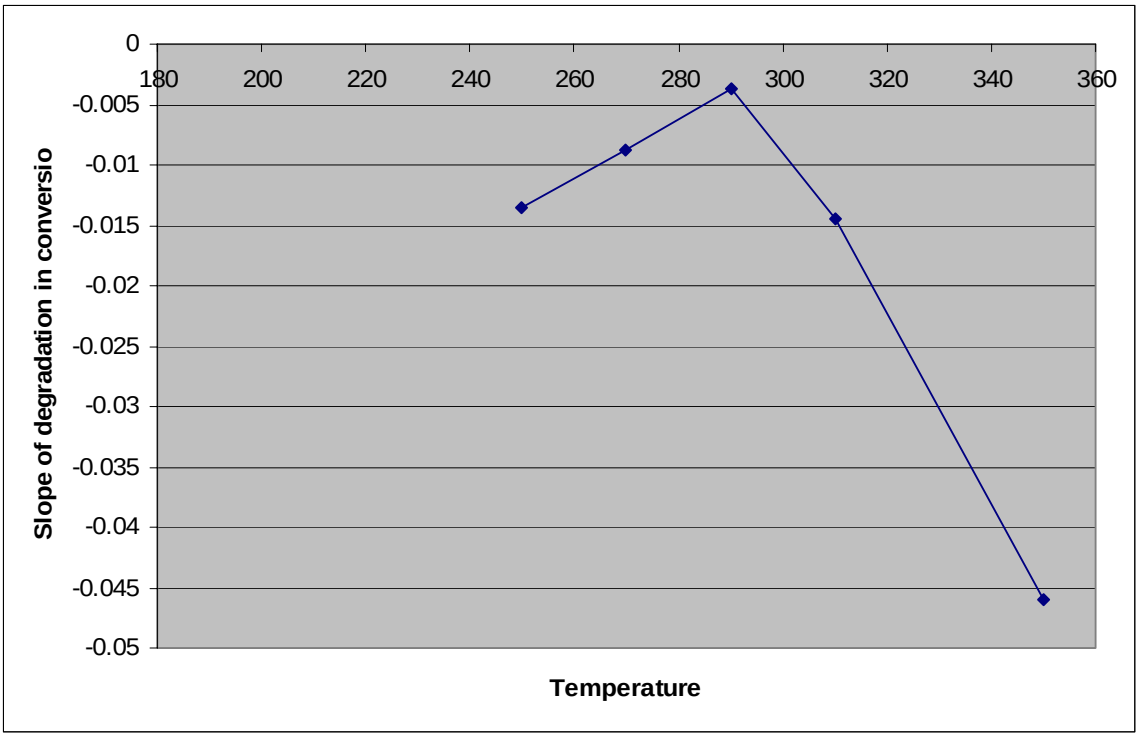

Figure 9: Decrease in catalyst effectiveness at various temperatures

Reformer Transient Response

Figure 10 shows the reactor temperature as the flow rate changes from low flow to high flow. At the 9 minute mark, the flow rate increases and the centerline temperatures drop immediately. It is interesting to note that the Zone 4 temperature rises for about a minute before dropping. There is currently not enough information to know why this occurs. Reactor temperatures reach their lowest point after about 5 minutes, and then increase a small amount before going into steady state. At the 24 minute mark, the flow rate decreases and the centerline temperatures rise, although not as quickly as they fell. Steady state conditions are reached after about 10 minutes.

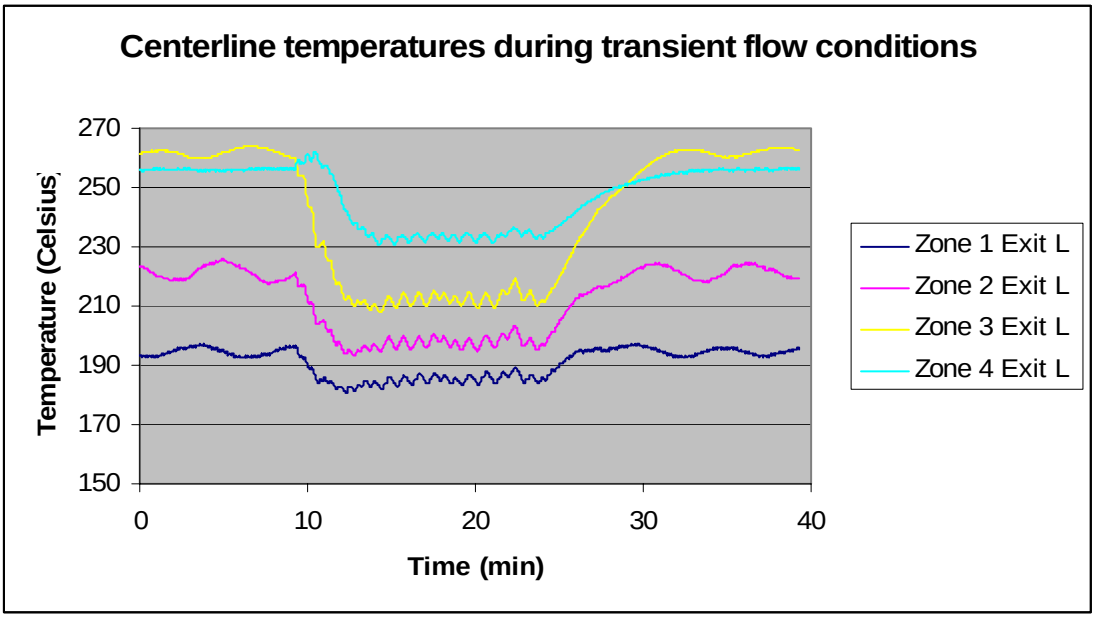

Figure 10: Reactor temperature during one cycle from low flow to high flow to low flow again

Methanol conversion was also measured during this experiment as shown in Table 2. The conversion percentage at high flow rate was measured before and after the transient period to insure that no catalyst degradation occurred during the test. The last row in the table is the estimated conversion percentage from 30 minutes of steady state operation at low flow plus 30 minutes of steady state operation at high flow. Again, due to slow transient response, it was expected that some methanol would escape unconverted when the flow changes from low to high. The data obtained does show this to be true; however, the differences may be within the error limits. This experiment needs to be repeated to verify that the results are statistically significant.

Table 2: Methanol conversion during the experiment

Conversion at 5 ml/min	98.09%
Conversion over 60 minutes of transient flow (2 cycles)	98.62%
Conversion at 5 ml/min	98.12%
Conversion at 2.5 ml/min	100.21%
Theoretical transient conversion using steady state data	98.81%

CONCLUSION

Degradation tests have begun using the flow disturbance disks and rings sets referred to as bluff bodies. As the bluff body set up has shown increased conversion of fuel as noted in past reports, it is expected that the flow disturbers will also have an effect in decreasing catalyst degradation rates. The first set of data has been collected regarding the use of coal based methanol with the bluff body set up. The degradation rates are much higher in this reactor than with the previous smaller reactors used for testing catalyst deactivation. In comparison to catalyst degradation due to the differences in fuel type (fuel cell grade vs coal derived methanol) as reported previously, it appears that the effect of reactor geometry on catalyst degradation far outweighs the effect of fuel type. This is an encouraging result for those eager to use coal-derived methanol as a hydrogen feed-stock. Future work is necessary to further quantify the effect of geometry in catalyst degradation.

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Several research publications showing the results of using coal-derived methanol in steam reformation are now in review. If approved, these results will be presented at the 2005 ASME Heat Transfer Conference and the 2005 National Hydrogen Association Annual Conference.

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